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BATTERY SEPARATOR FROM POLYPHENYL QUINOXALINE POLYMER BLENDS

BY DR. ISAAC ANGRES

RESEARCH AND TECHNOLOGY DEPARTMENT

APRIL 1978

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SUMMARY

This investigation is a continuation of the development of a heat and oxidation resistant battery separator. It is established that a combination of polyphenyl quinoxaline with cellulose acetate provides a potentially useful battery separator. The work is being performed under NAVSEA Task Number SF 43431302 and NAVSEC Task Number 6157D-1001.

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INTRODUCTION

One of the problems associated with conventional alkaline batteries (i.e., AgO-Zn, Ni-Zn) is that the battery separator of choice, cellophane, undergoes oxidative degradation during long-term storage and operation.^{1,2}

In addition to the standard characteristics required for normal battery operation, an improved separator should have the following characteristics:

1. Diffusion rates comparable to cellophane;
2. Specific resistance comparable to that of cellophane.
3. Hydrolytic and oxidative stability in 31% KOH and 45% KOH solutions under operating conditions.

This paper describes the preparation of new heat resistant separators based on blends containing polyphenylquinoxaline (PPQ), an aromatic polymer, as the matrix.

EXPERIMENTAL

The polyphenylquinoxaline (PPQ) polymer was prepared according to the method of Stille.³ The reported inherent viscosity for this polymer is 2.05 dl/g, and the glass transition temperature is 420°C.⁴ Cellulose acetate (CA) (39.8% acetyl content), cellulose triacetate (CT), polyvinylacetate (PVAc), and polyvinylpyrrolidone (PVP) were all obtained from Aldrich Chemical Company.

SEPARATOR PREPARATION

The following procedure applies to all of the above polymers when blended with the PPQ and using chloroform as the solvent: 30g of a 10% PPQ solution in m-cresol was added to a suitable container followed by the addition of 2g of any polymer (CA, CT, PVAc, PVP) or 2g of a mixture of the above polymers. To the above mixture there was added 100ml of chloroform and the resulting composition was stirred thoroughly until a homogeneous solution was obtained. The homogeneous solution was used for casting purposes.

1. Fleisher, A. and Lamden, J. J., Editors, "Zinc-Silver Oxide Batteries", John Wiley & Sons, New York, N.Y. 1971, pp. 263-269.
2. "Proceedings of the Symposium on Battery Separators", the Electrochemical Society, February 18-19, 1970, Columbus, Ohio.
3. Stille, J. K., U.S. Patent No. 3,661,850, May, 1972.
4. Hergenrothen, P. and Levine, H., J. Polymer Science, A-1 5, 1453 (1967).

Following the casting of the film, (i.e., on a suitable glass plate) the solvent was allowed to evaporate slowly for about 2-3 minutes by partially enclosing the plate with a plastic container. The plate was then immersed in a 1:1 methanol-water bath, and allowed to stand for ten minutes. The film was washed with water and dried in air.

RESISTANCE AND DIFFUSION MEASUREMENTS

Resistance measurements were made using the method of Kilroy and Moynihan.⁵ Hydroxyl diffusion measurements were performed using the method of Harris.⁶

STABILITY MEASUREMENTS

DIMENSIONAL. Rectangular pieces (approximately 50 x 60 mm) of membranes were cut and accurately weighed after equilibration at ambient laboratory conditions. The sample was then accurately measured with calipers and a micrometer to determine its true dimensions.

The specimens were then placed in vials which contained 45% by weight of KOH and stored at 25°C or 80°C. The specimens were removed from the alkali solution at regular intervals and after blotting the excess solution, were again accurately measured and weighed. The results were recorded over a period of 28 days and are reported as percent change.

CHEMICAL. The chemical stability in the silver-zinc battery environment was evaluated in a qualitative fashion by visual observation of exposed specimens. Samples (0.5x3 cm) were cut and immersed in a 45% solution of KOH which had been saturated with AgO. The samples were placed in an oven at 80°C and removed at regular intervals for inspection. Samples which had changed color or had become deformed or brittle were judged to be chemically unstable.

RESULTS AND DISCUSSION

PPQ is a nonpolar polymer hydrophobic to the KOH electrolyte with a high inherent electrical resistance. In order to reduce the electrical resistance, polymers such as polyvinylpyrrolidone, cellulose acetate, cellulose triacetate, and polyvinylacetate which are polar and hydrophilic were incorporated to form codispersed heterogeneous membranes. The polar component was removed by extraction in a suitable solvent or hydrolysis in 45% KOH in order to create a semiporous film consisting of a PPQ matrix with an unknown amount of the more polar polymer remaining.

5. Kilroy, W. P. and Moynihan, C., J. Electrochem. Soc., 125, 0000 (1978).
6. "Characteristics of Separators for Alkaline Silver Oxide-Zinc Secondary Batteries - Screening Methods", Edited by Cooper, J. E. and Fleisher, A., AD-447301, Chapter 9, pp. 92-102.

By blending PPQ (60%) in chloroform solution with the other polymers (40%), polymeric membranes were obtained which showed promise for use as battery separators. The resistance and thickness of several codispersed membranes are illustrated in Table 1.

Table 1 suggests that a combination of PPQ with cellulose acetate gives the membrane with the lowest resistance thereby making it the separator of choice. We found that after heating for three months at 80°C in a 45% KOH solution saturated with silver(II)oxide, the PPQ/CA separator remained intact with no appreciable deterioration while the cellophane deteriorated after 16 hours.

The dimensional changes were compared with cellophane and plotted as percentage change versus time. The results are illustrated in Figures 1, 2, and 3. As expected, the hydrophilic cellophane has absorbed KOH electrolyte to more than double its thickness. Similarly, this is observed in the weight changes in cellophane. The large percentage weight increase in cellophane compared to PPQ or PPQ/X-polymer is in agreement with its hydrophilic nature and the dimensional change in its thickness.

Figure 4 illustrates the relative rates of achieving constant resistance for cellophane and PPQ/CA. The speed (10 minutes) at which cellophane achieves constant resistance is again in agreement with its hydrophilic nature. It takes approximately nine times longer for PPQ/CA to achieve constant resistance indicating the PPQ matrix together with cellulose acetate is not as hydrophilic as cellophane.

The diffusion of OH^- ions through the separator was studied by following the pH changes across the separator by the method of Harris.⁶ The flux of OH^- ions was calculated according to the expression.⁶

$$\text{FLUX} = \frac{\Delta M}{A \Delta t} = \frac{\Delta C}{\Delta t} \times \frac{V}{A} \text{ (Moles/unit time-unit area)}$$

The results of the diffusion studies across several membranes are represented in Figure 5. Hydroxyl ion diffusion is faster through cellophane than for PPQ/CA. The average flux of OH^- ions through cellophane was 1.61×10^{-3} mole/min-square inch whereas the flux for PPQ/CA was 1.06×10^{-3} mole/min square inch. The differences in fluxes are readily accounted for by the fact that at the molecular level cellophane comes close to a heterogeneous molecular sieve,⁷ and at the same time its intra-molecular hydrogen-bonded interactions allows for wettability and diffusion to occur somewhat faster. The slower flux for PPQ/CA can be explained by the non-polar and hydrophobic nature of the PPQ. Similarly, it will be immediately appreciated that it is the cellulose acetate that provides the basis for wettability and electrolyte flow.

7. Daniels, F. K., "Dialysts" in Kisk-Othmer "Encyclopedia of Chemical Technology", 1st Ed., Interscience, N. Y. 1950.

Table 1. Properties of PPQ Composite Membranes

MEMBRANE ^a	RESISTANCE IN 45% KOH ohm-cm	FILM THICKNESS MILS	
		DRY	IN 45% KOH
PPQ/CA	40	1.3	2.1
	55	1.8	2.8
	60	1.7	2.9
PPQ/CT	100	2.2	3.5
	150	2.8	4.0
	125	2.1	3.3
PPQ/PVA	200	1.1	2.1
	230	1.4	1.9
	280	1.8	2.7
PPQ/PVP	> 1000	1.0	1.4
	> 1000	0.7	1.0
	> 1000	0.4	0.6

a. THE RATIO OF PPQ/X-POLYMER IS 60/40

CONCLUSION

It has been shown that an aromatic heterocyclic polymer such as polyphenylquinoxaline, can be blended with CA to produce potential battery separators.

ACKNOWLEDGEMENT:

This task was performed under support from the Naval Sea Systems Command and the Department of Energy. We wish to thank Al Himy for his useful discussions and suggestions.

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1. Fleisher, A. and Lamden, J. J., Editors, "Zinc-Silver Oxide Batteries", John Wiley & Sons, New York, N.Y. 1971, pp. 263-269.
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7. Daniels, F. K., "Dialysts" in Kisk-Othmer "Encyclopedia of Chemical Technology", 1st Ed., Interscience, N. Y. 1950.

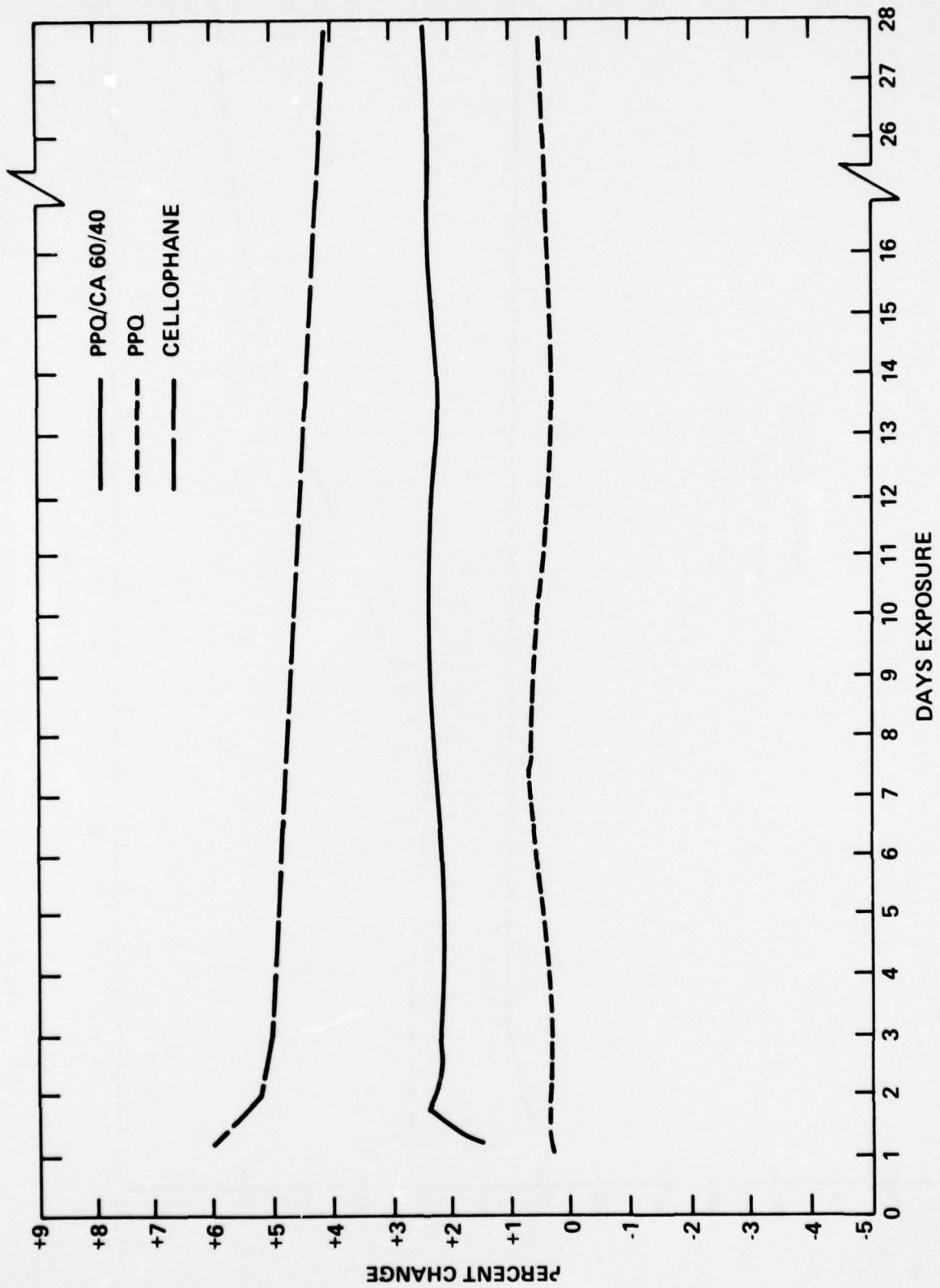


FIGURE 1 DIMENSIONAL CHANGE (L x W) VS EXPOSURE TIME IN 45% KOH AT 25°C

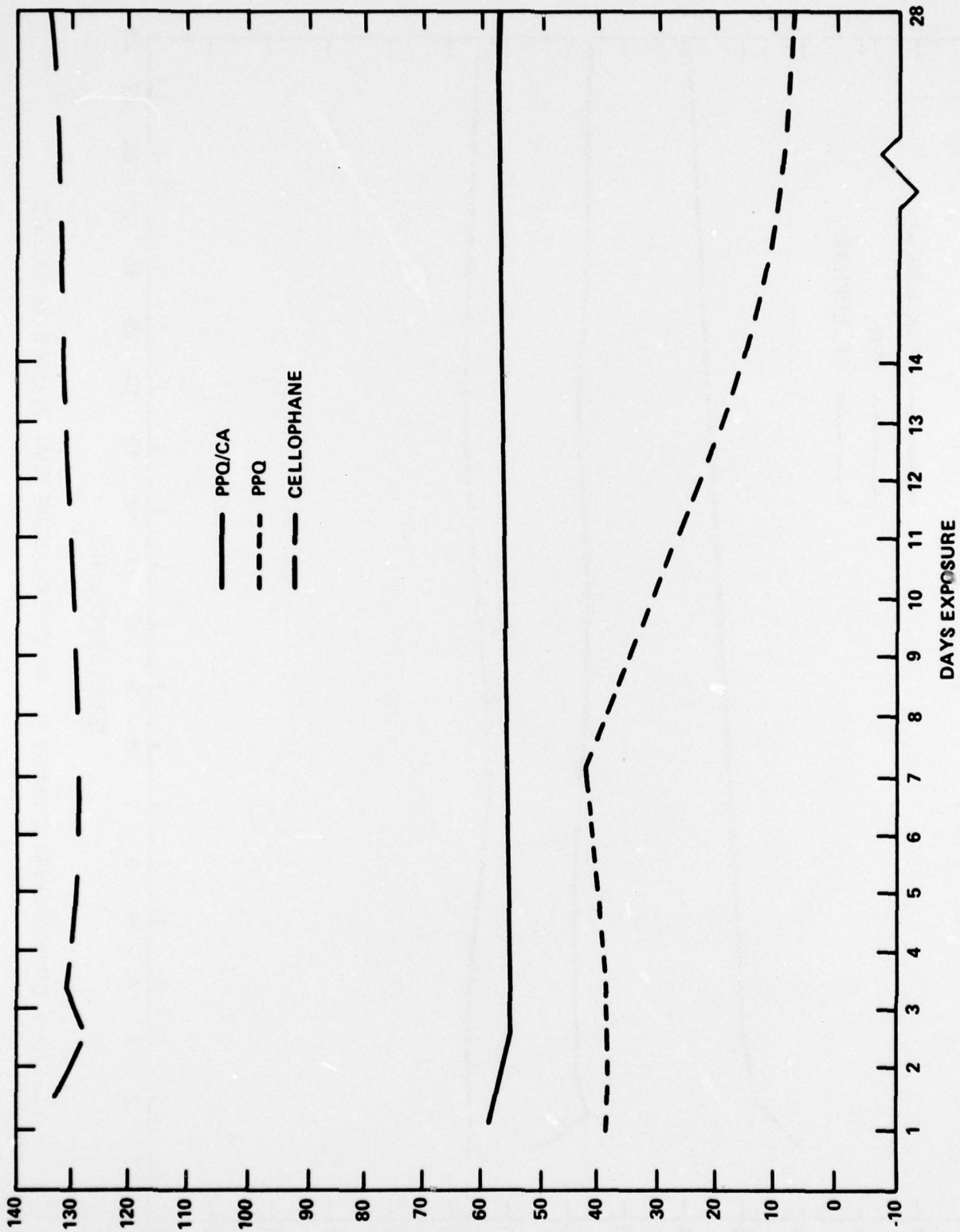


FIGURE 2. DIMENSIONAL CHANGE (THICKNESS) VS EXPOSURE TIME IN 45% - KOH AT 25 °C

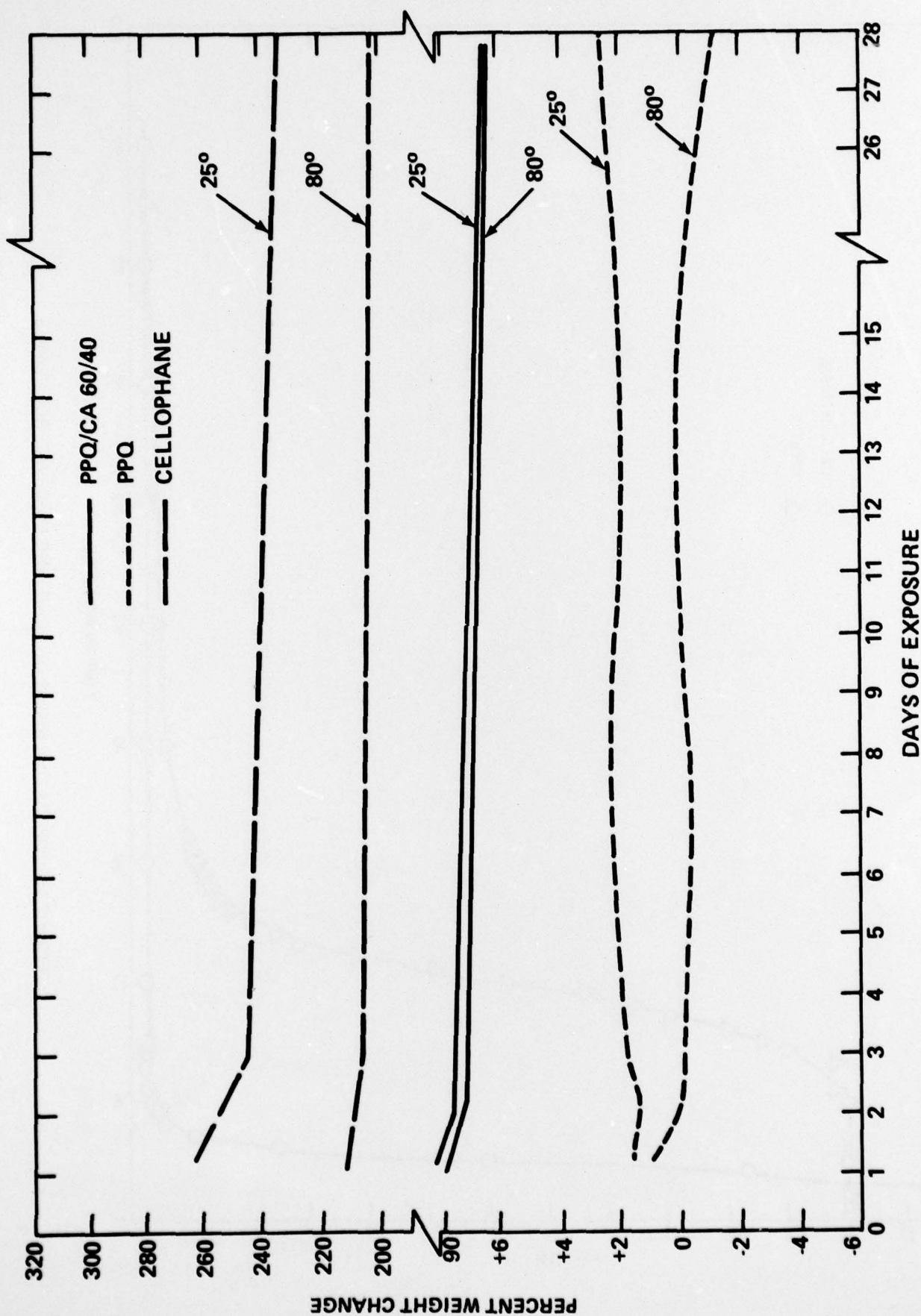


FIGURE 3 WEIGHT CHANGE VS EXPOSURE TIME IN 45% KOH AT 25° AND 80°C

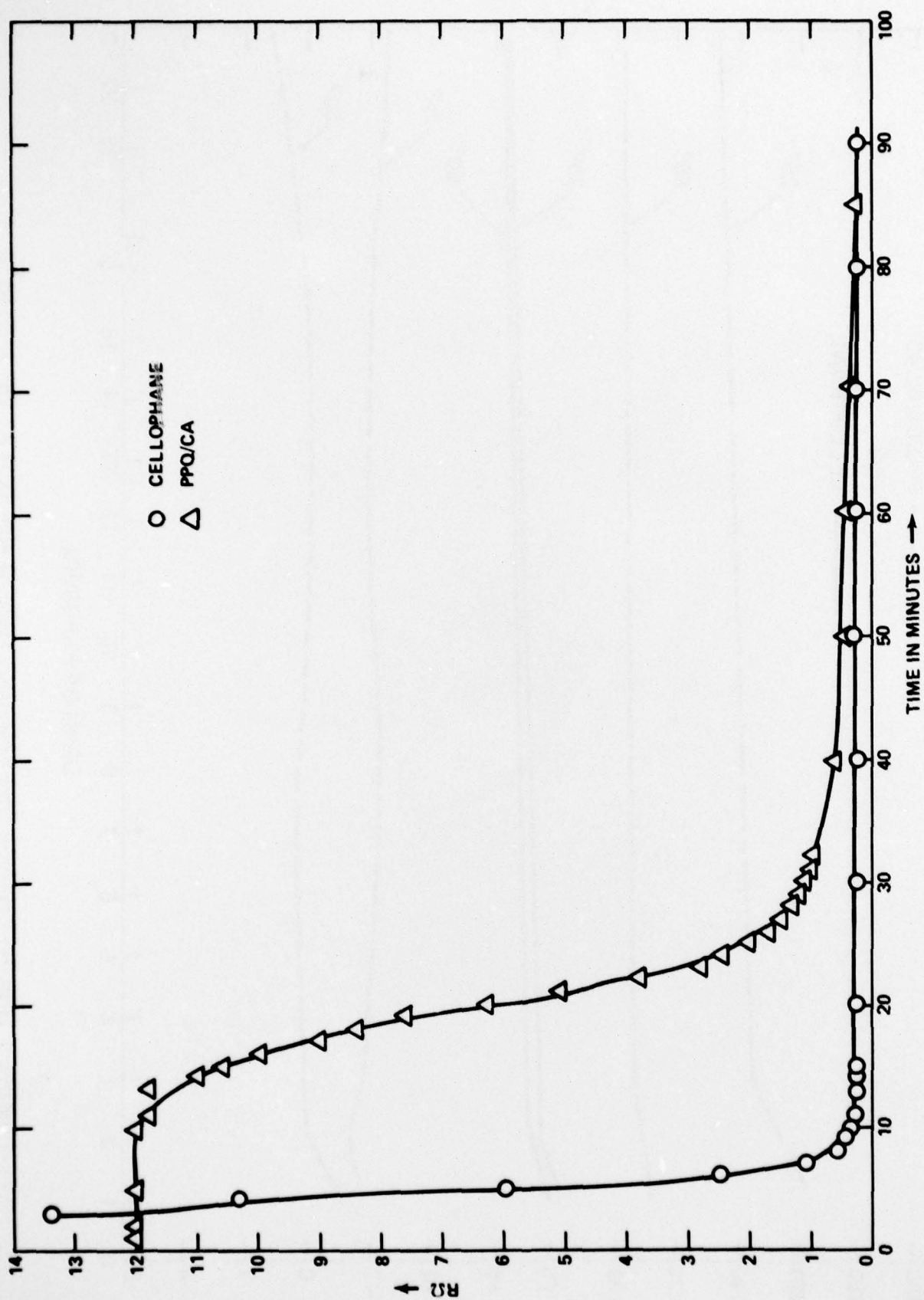
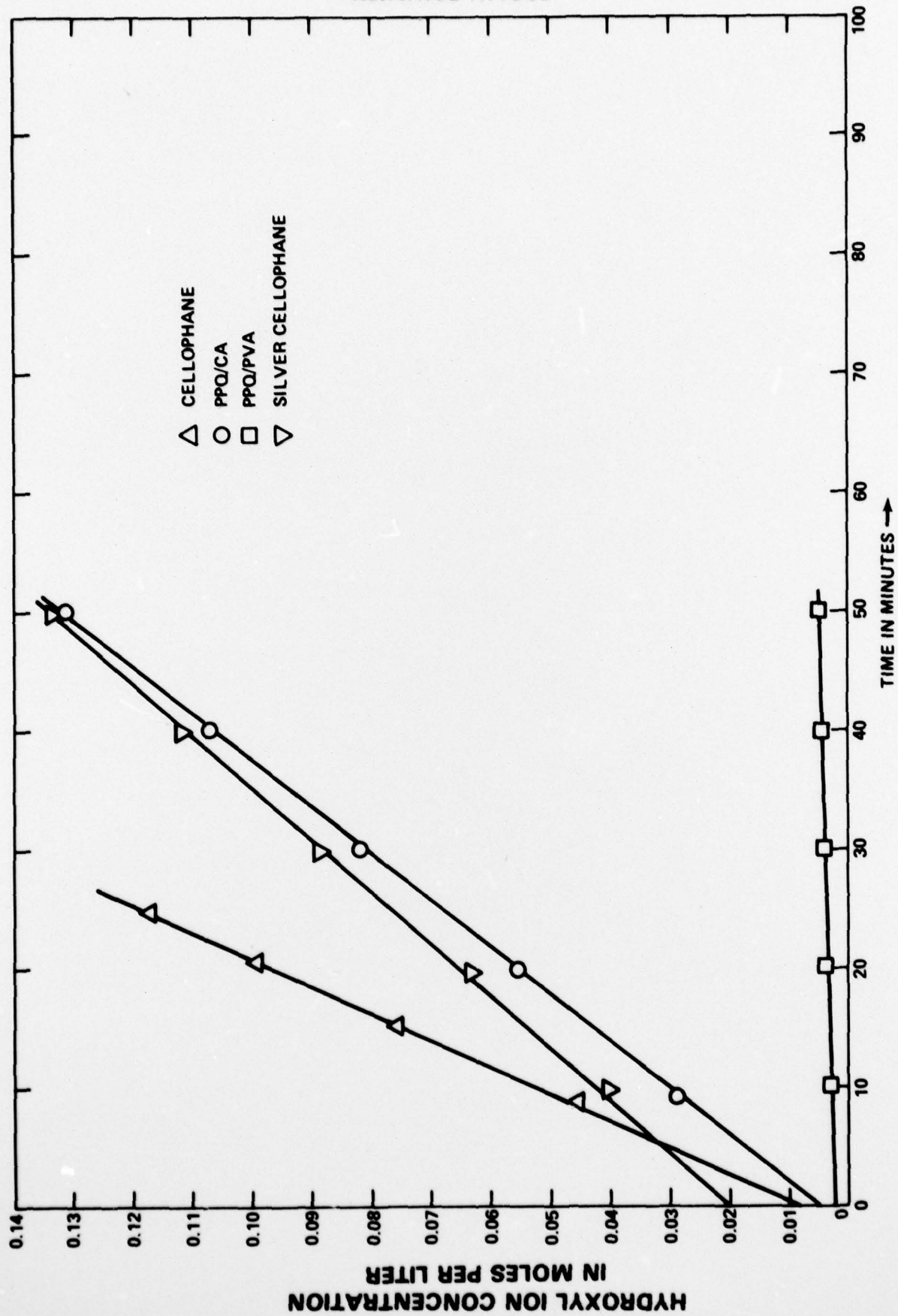


FIGURE 4 COMPARATIVE RATES OF ACHIEVING CONSTANT RESISTANCE

FIGURE 5 DIFFUSION OF OH⁻ THROUGH SEVERAL MEMBRANES

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